Chemical erosion: why is ocean salty?

Finally, we turn our attention to the dissolved load in the rivers — the source of the ocean's saltiness.

Recall first — Fig. 5.3 — the main dissolved species in river water

Ca^{++}, Mg^{++}, Na^{+} — main cations

talk about pollution page 1.5 here

Cl^{-}, $SO_4^{=}$, HCO_3^{-} — main anions

These are also the main ions in seawater — nonestuarine seawater has a very constant chemical composition — Table 8.1

Total dissolved solids 35 g/kg

Salinity = 35 ‰ parts per mille (parts per thousand)

Knowing the average concentration of each species in river water, the concentration in seawater, and the rate of H_2O addition to the oceans from all the world's rivers, can calculate the replacement times τ for each species.

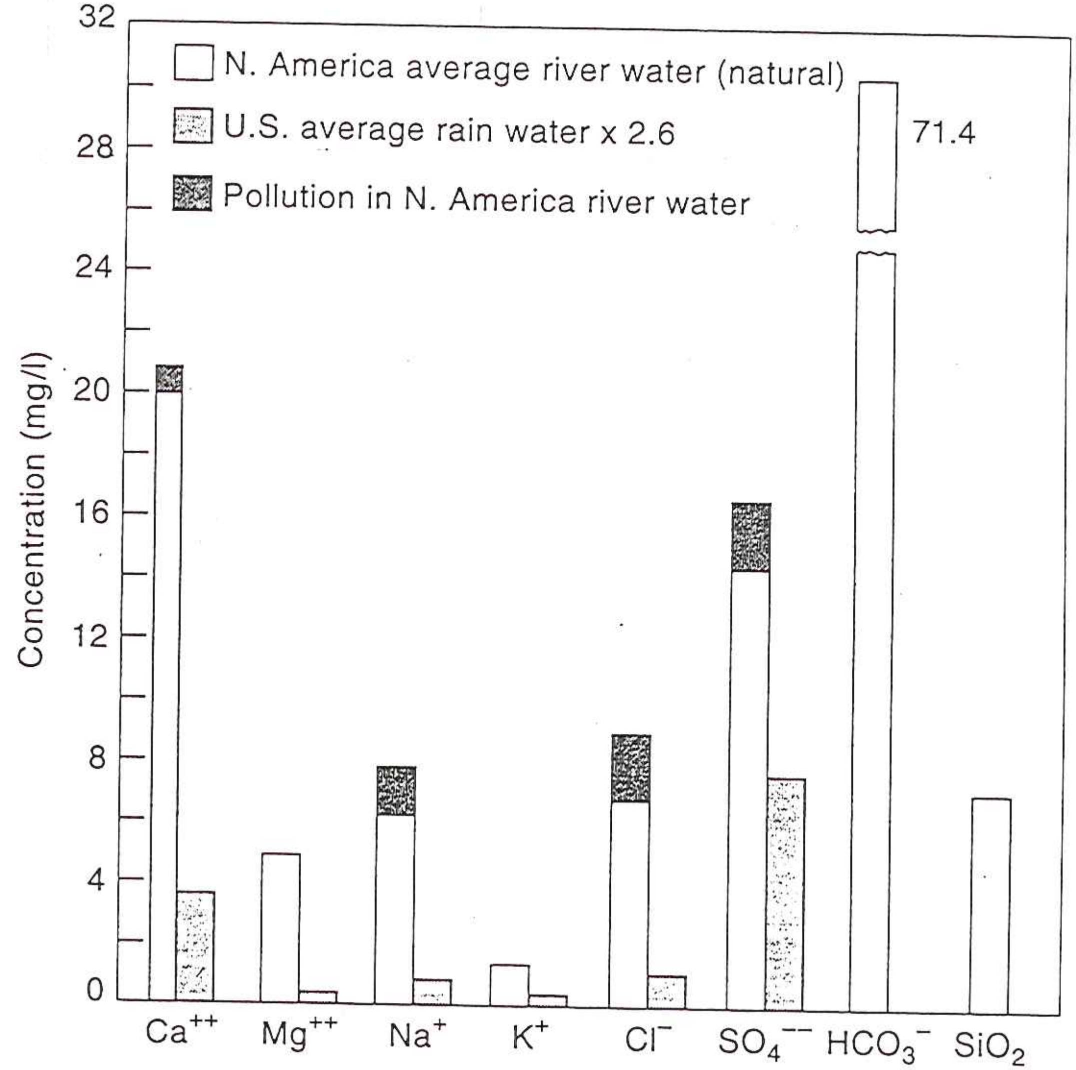


Figure 5.3. Comparison of dissolved composition of North American natural and polluted river water (data from Meybeck 1979) with U.S. rainwater (concentrations in mg/l). Rainwater concentrations are multiplied by 2.6 to correct for evaporation from the continents (see text).

TABLE 5.6 Chemical Composition of Average River Water

By Continent	River Water Concentration[a] (mg/l) Ca^{++}	Mg^{++}	Na^+	K^+	Cl^-	SO_4^{--}	HCO_3^-	SiO_2	TDS	Water Discharge (10^3 km^3/yr)	Runoff Ratio[b]
Africa:											
Actual	5.7	2.2	4.4	1.4	4.1	4.2	26.9	12.0	60.5	3.41	0.28
Natural	5.3	2.2	3.8	1.4	3.4	3.2	26.7	12.0	57.8		
Asia:											
Actual	17.8	4.6	8.7	1.7	10.0	13.3	67.1	11.0	134.6	12.47	0.54
Natural	16.6	4.3	6.6	1.6	7.6	9.7	66.2	11.0	123.5		
S. America:											
Actual	6.3	1.4	3.3	1.0	4.1	3.8	24.4	10.3	54.6	11.04	0.41
Natural	6.3	1.4	3.3	1.0	4.1	3.5	24.4	10.3	54.3		
N. America:											
Actual	21.2	4.9	8.4	1.5	9.2	18.0	72.3	7.2	142.6	5.53	0.38
Natural	20.1	4.9	6.5	1.5	7.0	14.9	71.4	7.2	133.5		
Europe:											
Actual	31.7	6.7	16.5	1.8	20.0	35.5	86.0	6.8	212.8	2.56	0.42
Natural	24.2	5.2	3.2	1.1	4.7	15.1	80.1	6.8	140.3		
Oceania:											
Actual	15.2	3.8	7.6	1.1	6.8	7.7	65.6	16.3	125.3	2.40	—
Natural	15.0	3.8	7.0	1.1	5.9	6.5	65.1	16.3	120.3		
World average:											
Actual	14.7	3.7	7.2	1.4	8.3	11.5	53.0	10.4	110.1	37.4	0.46
Natural (unpolluted)	13.4	3.4	5.2	1.3	5.8	8.3 (5.3)[c]	52.0	10.4	99.6	37.4	0.46
Pollution	1.3	0.3	2.0	0.1	2.5	3.2 (6.2)[c]	1.0	0	10.5	—	—
World % pollutive	9%	8%	28%	7%	30%	28% (54%)[c]	2%	0%	—	—	—

road salt

fertilizer + coal

[a] *Actual* concentrations include pollution. *Natural* concentrations are corrected for pollution.

[b] Runoff ratio = average runoff per unit area/average rainfall (calculated from Meybeck).

[c] We have raised pollutive contribution; see Table 5.11. (Our values are in parentheses.)

Source: All river water concentrations and discharge values from Meybeck (1979) except "actual" concentrations by continent, which were calculated from Meybeck's data. (M. Meybeck, "Concentrations des eaux fluviales en éléments majeurs et apports en solution aux oceans," *Rev. Géol. Dyn. Georgr. Phys.*, 21(3), 220, 227.

Table 5.6 — continent by continent breakdown

Briefly discuss two major sources of pollution

- Na^+ Cl^- road salt in winter
- SO_4^{--} fertilizer added to fields
  from sulfuric acid used in their production
  also from ~~[illegible]~~ coal combustion

TABLE 8.1 Major Dissolved Components of Seawater for a Salinity of 35‰

Ion	Concentration g/kg	mM[a]	Percent Free Ion
Cl^-	19.354	558	100
Na^+	10.77	479	98
Mg^{++}	1.290	54.3	89
SO_4^{--}	2.712	28.9	39
Ca^{++}	0.412	10.5	99
K^+	0.399	10.4	98
HCO_3^{-}[b]	0.12	2.0	80

[a] mM = millimoles per liter at 25°C.

[b] For pH = 8.1, P = 1 atm, T = 25°C.

Sources: Wilson 1975; Skirrow 1975; Millero and Schreiber 1982.

TABLE 8.3 Replacement Time with Respect to River Addition, τ_r, for Some Major and Minor Dissolved Species in Seawater

Component	Concentration (μM) River Water	Seawater	τ_r[a] (1,000 yr)
Cl	230	558,000	87,000
Na^+	315	479,000	55,000
Mg^{++}	150	54,300	13,000
SO_4^{--}	120	28,900	8,700
Ca^{++}	367	10,500	1,000
K^+	36	10,400	10,000
HCO_3^-	870	2,000	83
H_4SiO_4	170	100	21
NO_3^-	10	20	72
Orthophosphate	1.8	2	40

[a] τ_r = ([SW]/[RW]) τ_w, where τ_w = replacement (residence) time of H_2O = 36,000 yr; RW = river water; SW= seawater, and [ ] = concentration in μmoles per liter = μM.

Example : Cl — chlorine Cl^-

volume of oceans $= 4\pi\,(6371)^2\,(0.7)(4)$

$= 1.4 \cdot 10^9\ km^3$

$= 1.4 \cdot 10^{21}$ liters

moles Cl in oceans =

$(1.4 \cdot 10^{21}\ \ell)\left(.558\ \frac{moles}{\ell}\right)$

$= 7.8 \cdot 10^{20}$ moles Cl in oceans

Rate of addition by Cl in rivers:

37,400 km^3 H_2O / yr all rivers

$= 3.7 \cdot 10^{16}\ \ell\ H_2O$ / yr

Chlorine addition : note: very small — fresh water

$3.7 \cdot 10^{16}\ \frac{\ell\ H_2O}{yr} \times 230 \cdot 10^{-6}\ \frac{moles}{\ell}$

$= 8.5 \cdot 10^{12}$ moles Cl added / yr

Replacement time $\tau = \frac{7.8 \cdot 10^{20}\ moles}{8.5 \cdot 10^{12}\ moles/yr} =$ 90 million years

Berner finds 87 million

Such estimates used as as estimate of age of ⊕ before modern knowledge.

Note — the replacement time for Ca^{++} is much less than for Cl — this the basis of a homework problem in Part I of this course

Table 5.12 shows the source minerals for the two most important cations

Ca mostly from sedimentary rocks

Most Ca is derived from $CaCO_3$ limestone, but also some from dolomite and some from plagioclase

Mg comes from dolomite, but more than half from Mg silicates — weathering of igneous rocks

Table 5.13 shows the sources of the most important anion HCO_3^-

- 64 % from solution of atmospheric CO_2 in pore spaces
- 34 % calcite + dolomite
- 2 % pollution

TABLE 5.12 Sources of Ca and Mg in World Average River Water

Source	Percent of Total Ca	Percent of Total Mg
Weathering		
Calcite, $CaCO_3$	52	—
Dolomite, $CaMg(CO_3)_2$	13	36
$CaSO_4$ minerals	8	—
Ca-silicates (plagioclase)	18	—
Mg-silicates	—	54
Cyclic sea salt	<<1	2
Pollution	9	8
Total	100	100

Source: Data for rock sources from Berner et al. 1983. Cyclic sea salt from Table 5.10 and pollution from Meybeck 1979.

TABLE 5.13 Sources of Rock Weathering-Derived HCO_3^- in World Average River Water

Weathering Source	Percent of Total HCO_3^- from Soil CO_2	Percent of Total HCO_3^- from Carbonate Minerals
Calcite + Dolomite	27	34
Ca-silicates	13	—
Mg-silicates	15	—
Na-silicates	6	—
K-silicates	3	—
Total	64	34

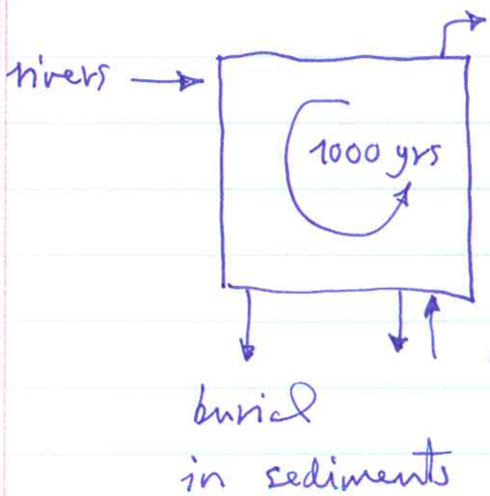
Note: For method of calculation, see text. (An additional 2% of total HCO_3^- is added by pollution; see Table 5.11.)

So... why are all the replacement times so much shorter than the age of the Earth — answer: there must be sinks.

Geochemist box models — Fig. 8.3 — try to identify all sources & sinks — major element cycling

Main input from rivers — dissolved load

Other arrows in Fig. 8.3



→ marine aerosol formation — sea breeze — can smell the salt near the oceans

reactions with volcanics — hydrothermal circulation at mid-ocean ridges — removes some elements but adds others

See figure & Table 8-8

- Mg^{++} removed from seawater
- Ca^{++}, however, is added

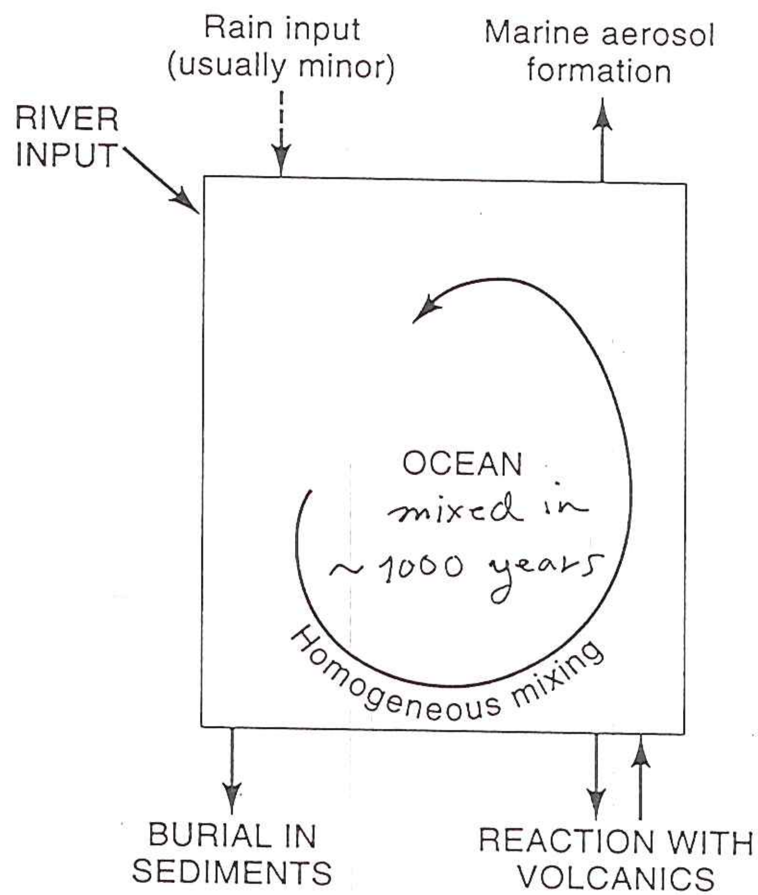


Figure 8.3. Simple box model appropriate for conservative elements in seawater. Note that, compared with the Sillèn model of Figure 8.2, fluxes enter and leave the box, and the atmosphere and sediments are considered to be outside the box. Also note that, in contrast to lakes, there is no outlet, so dissolved materials carried in by rivers can be removed only by sea–air transfer (marine aerosol formation), burial in sediments, or reaction with volcanics.

TABLE 8.12 Rates of Addition via Rivers of Major Elements to the ocean (as Dissolved Species) and Rates of Net Loss from the Ocean by Transfer of Sea Salt to the Continents via the Atmosphere

Species	Rate of Addition from Rivers[a] (Tg/yr)	Rate of Net Sea Salt Loss to Atmosphere (Tg/Yr)
Cl^-	308	40
Na^+	269	21
SO_4-S	143	4
Mg^{++}	137	3
K^+	52	1
Ca^{++}	550	0.5
HCO_3^-	1980	—
H_4SiO_4-Si	180	—

Note: $Tg = 10^{12}$ g.

[a] Based on river water input of 37,400 km^3/yr: includes pollution

Sources: River-water data from Meybeck 1979; cyclic salt data from Chapter 5.

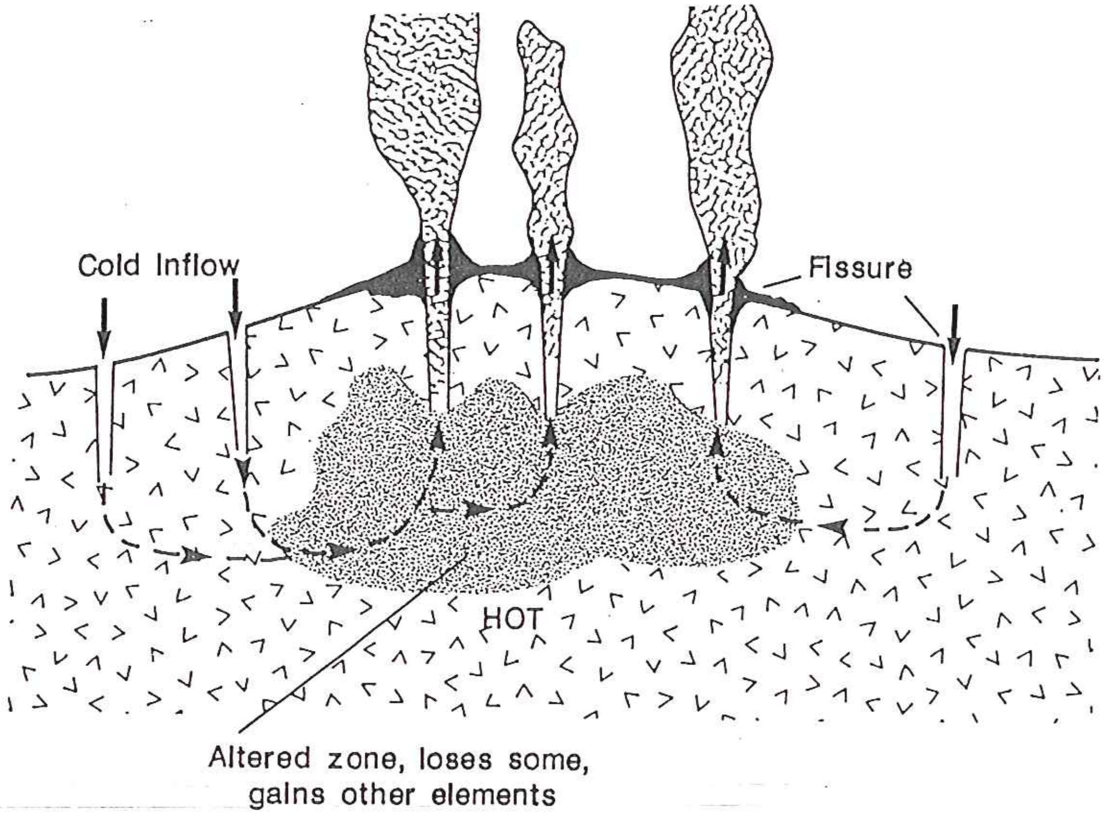


TABLE 8.8 Removal or Addition Fluxes of Some Major Seawater Constituents as a Result of Basalt-Seawater Reaction Near Midocean Ridges

	Flux (Tg/yr)		
Constituent	Edmond et al. (1979)	Thompson (1983)	Present Study
Mg^{++}	−187	−60	−119
Ca^{++}	140	73	191
K^{+}	51	−27	53
SO_4^{--} as S	−120	—	—[a]
H_4SiO_4 as Si	90	82	56

Note: Removal values shown as negative numbers. Tg = 10^{12}g.

[a] Less than 10% of Edmond et al. (1979) value

How do we know this? — By sampling of the hot plumes

Let's briefly consider ~~the~~ three elements

- Cl⁻ Chlorine — balance sheet

Table 8.13

215 Tg Cl^-/yr natural
93 pollution — road salt

Outputs much smaller — badly imbalanced at present time

Long-term balanced budget

- no road salt
- much more evaporite deposition in past — e.g. Gulf of Mexico — also Mediterranean Sea levels particularly high now — interglacial

- Mg^{++} magnesium

Before discovery of MOR hot springs, there was a serious imbalance problem now known that almost all Mg^{++} added by rivers (119 out of 137 Tg/yr) is removed by reactions with volcanic rock at ridges

• Ca^{++} calcium

Recall the differences between Ca^{++} and Mg^{++} from Table 8.3 (both same column periodic table)

	conc in river water (both μM)	conc in seawater
Mg^{++}	150	54,000
Ca^{++}	367	10,500

Much more Ca^{++} coming in rivers but much less present in oceans

Reason – Ca^{++} is preferentially incorporated into the shells of marine plankton – Figure 8.9

$CaCO_3$ shells

organisms grow in photic zone – top ~100m

Shell growth removes Ca^{++} from seawater
Die & sink to bottom

Berner's long term budget is balanced to within the uncertainties with which the various fluxes can be determined

Most input from rivers — some from hydrothermal geochemistry

Most output as $CaCO_3$ shells
- shallow water — shelves — coral reefs, etc.
- deep water — plankton

Below about 4 km depth the oceans are undersaturated w.r.t. $CaCO_3$
The solubility increases with presence

As a result deep-sea sediments below ~ 4 km depth are dissolved back into seawater — calcite compensation depth

See map of Atlantic Fig. 8.13

Think of mid-ocean ridges like "snow"-capped peaks

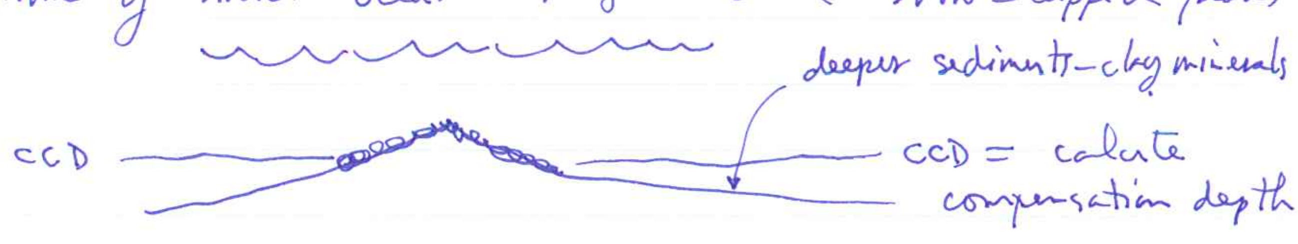


TABLE 8.13 The Oceanic Chloride Budget (Rates in Tg Cl^-/yr)

Present-Day Budget			
Inputs		Outputs	
Rivers (natural)	215	Net sea–air transfer	40
Rivers (pollution)	93	Pore-water burial	25
Total	308	Total	65
Long-Term (Balanced) Budget			
Inputs		Outputs	
Rivers	215	NaCl evaporative deposition	163
		Net sea–air transfer	40
		Pore-water burial	12
		Total	215

Note: Tg = 10^{12} g. Replacement time for Cl^- is 87 million years.

TABLE 8.16 The Oceanic Magnesium Budget (Rates in Tg Mg^{++}/yr)

(Balanced) Budget for Past 100 Million Years			
Inputs		Outputs	
Rivers	137	Volcanic–seawater reaction	119
		In biogenic $CaCO_3$	15
		Net sea–air transfer	3
		Total	137

Note: Tg = 10^{12} g. Replacement time for Mg^{++} is 13 million years.

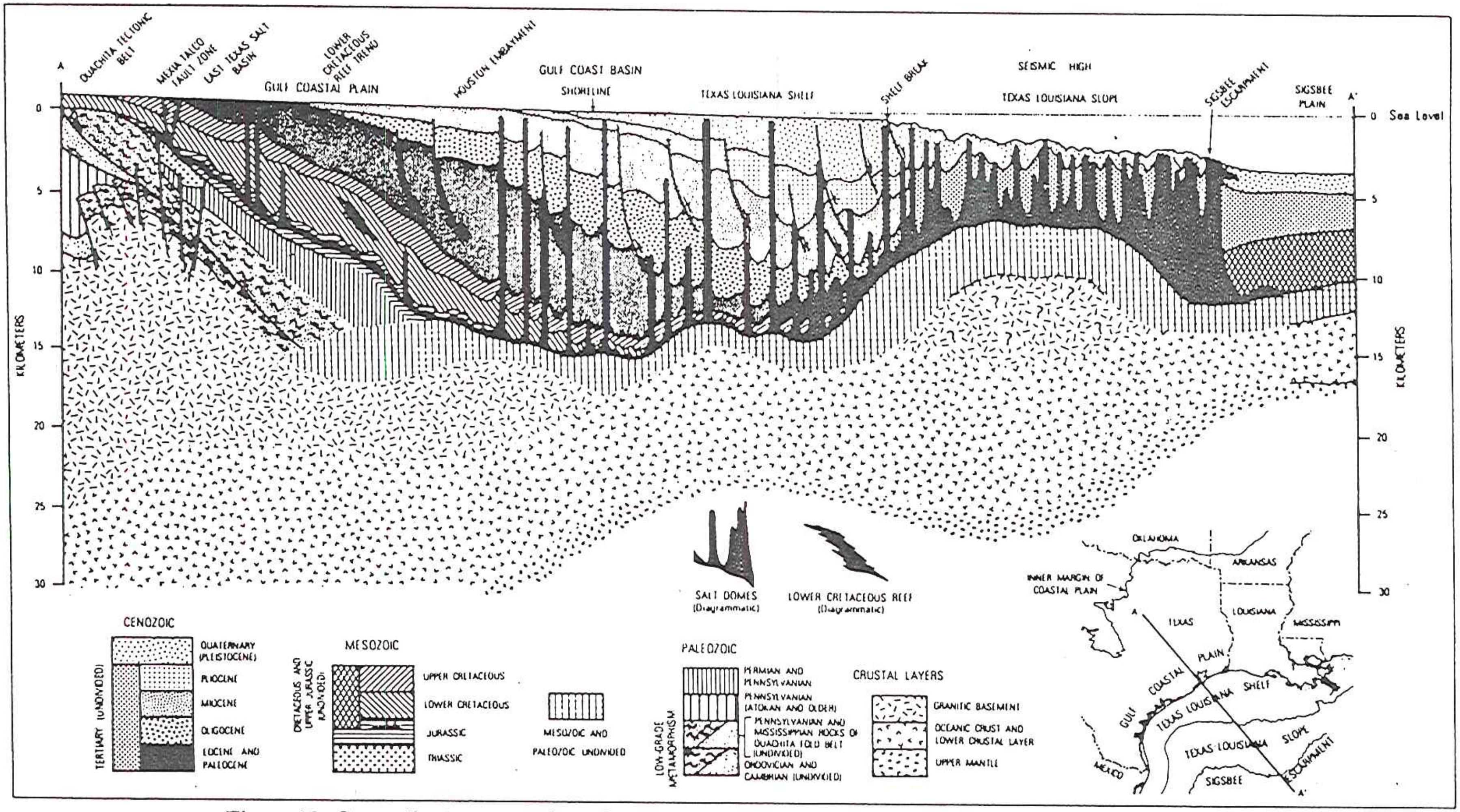


Figure 12. Generalized cross section of the northern Gulf of Mexico margin (from R. G. Martin, 1978, modified from earlier interpretations of Lehner, 1969; Dorman and others; 1972, Antoine and others, 1974; and Martin and Case, 1975).

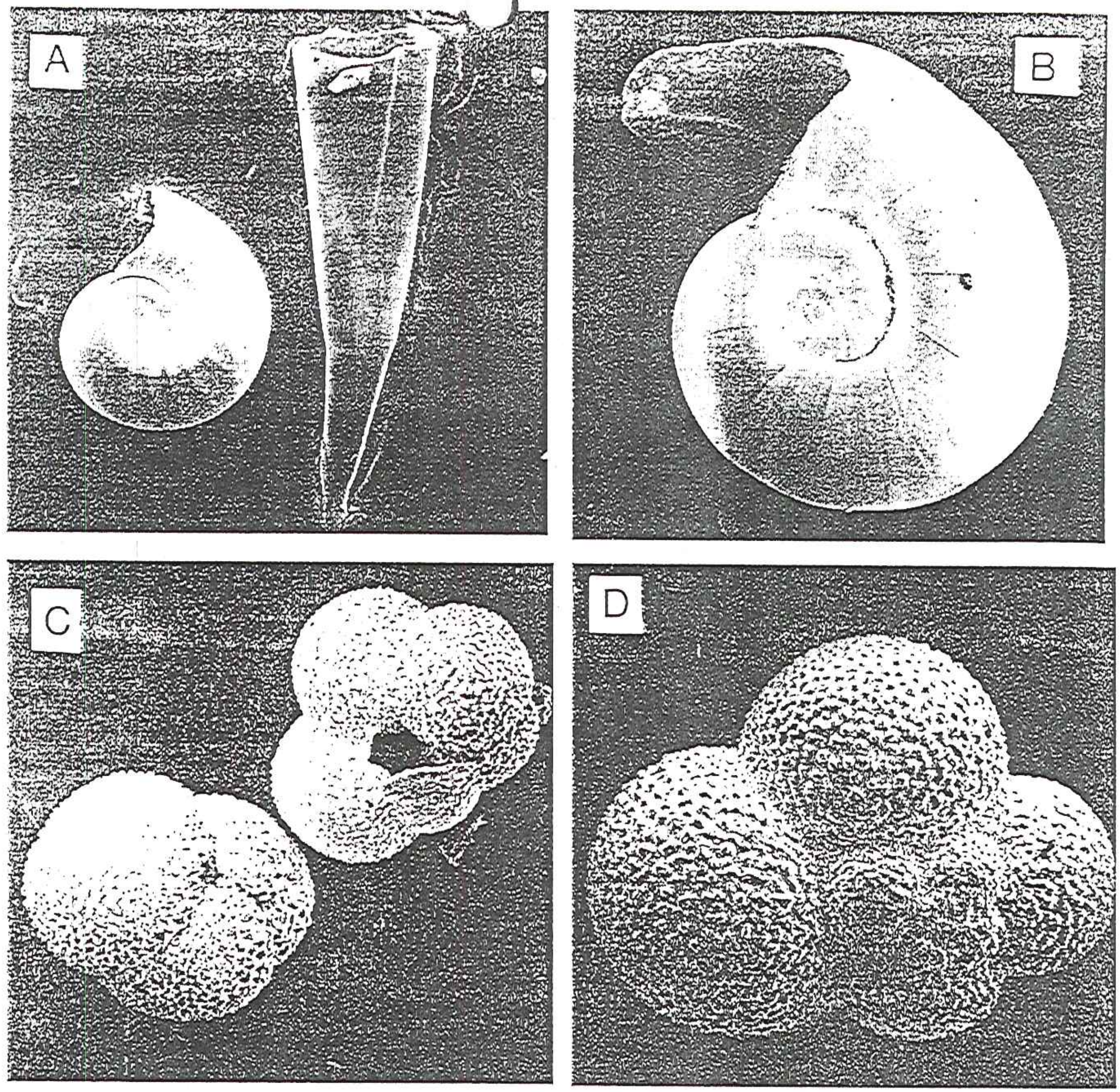


Figure 8.9. Photomicrographs of some planktonic $CaCO_3$-secreting organisms: (a) pteropod shells (aragonite) × 20; (b) pteropod shell (aragonite) × 10; (c) foram tests (calcite) × 70; (d) foram test (calcite) × 100.

TABLE 8.18 The Oceanic Calcium Budget (Rates in Tg Ca^{++}/yr)

Inputs		Outputs	
Present-Day Budget			
Rivers	550	$CaCO_3$ deposition:	
Volcanic–seawater reaction	191	Shallow water	520
Cation exchance	37	Deep sea	440
Total	778	Total	960
Budget for Past 25 Million Years			
Rivers	550	$CaCO_3$ deposition:	
Volcanic–seawater reaction	191	Shallow water	240
Cation exchance	19	Deep sea	440
		Evaporitic $CaSO_4$ deposition	49
Total	760	Total	729

Note: Tg = 10^{12} g. Replacement time (rivers only) for Ca^{++} is 1 million years.

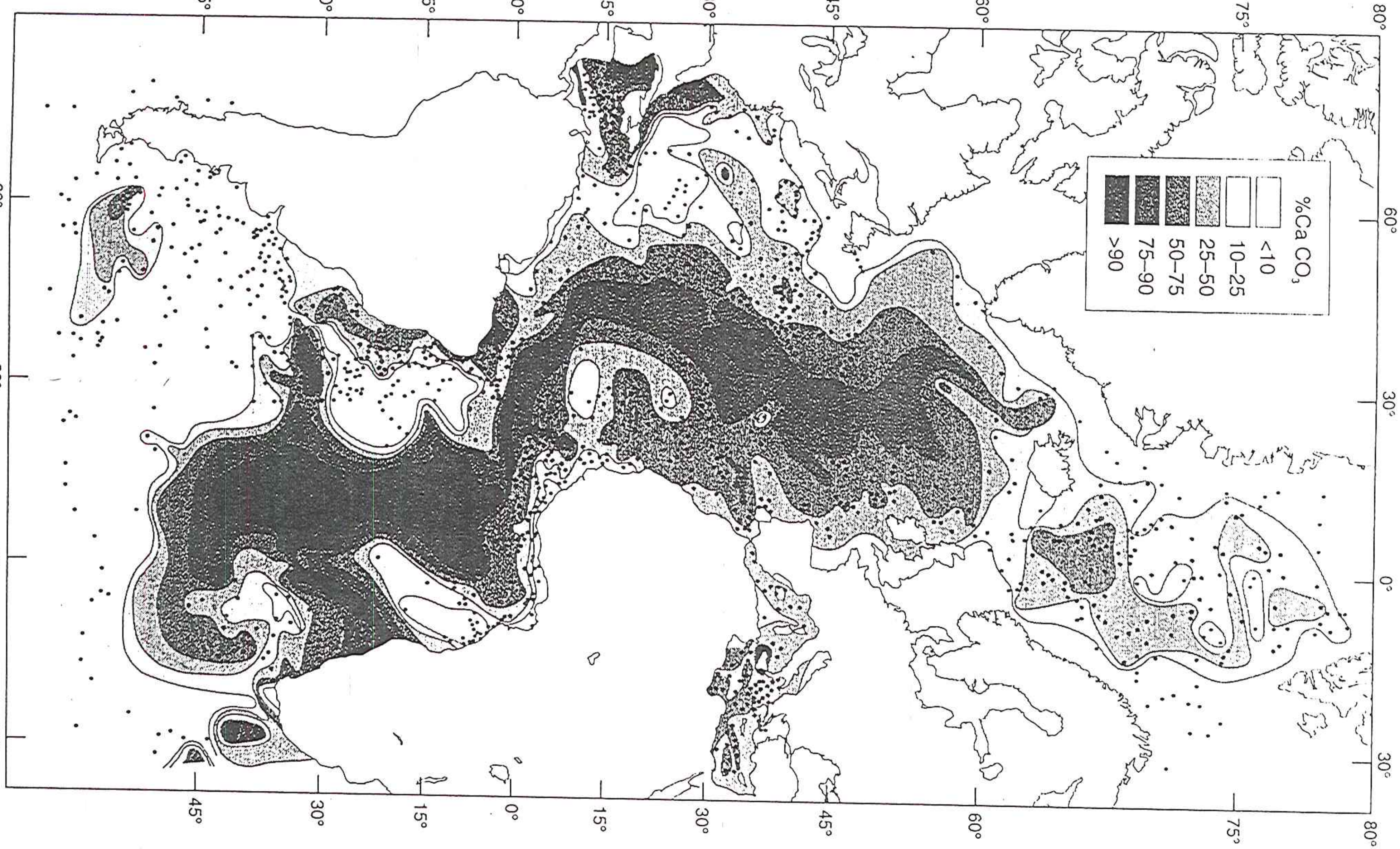


Figure 8.13. Distribution of $CaCO_3$ in deep-sea sediments of the Atlantic Ocean. Note that the highest concentrations are located at the shallowest depths atop the Mid-Atlantic Ridge. (After P. E. Biscaye, V. Kolla, and K. K. Turekian, "Distribution of Calcium Carbonate in Surface Sediments of the Altantic Ocean." *Journal of Geophysical Research* 81: 2596. Copyright © 1976 by the American Geophysical Union, reprinted by permission of the publisher.)